

***In situ* infrared measurements of a diamond electrochemical electrode during polarization**

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Using x-ray photoelectron spectroscopy (XPS), researchers have shown that boron doped diamond electrodes (polycrystalline and single crystal) gain oxygen upon electrochemical polarization in 0.5 M H_2SO_4 . XPS is an *ex situ* technique, however, so in addition to the possibility of contamination, it cannot provide any information on the character of the oxygen termination nor if the termination changes during the voltammogram cycle. To clarify this situation, we have investigated the nature of the oxygen termination of a diamond electrode surface using attenuated total reflectance infrared (ATR-IR) spectroscopy while the electrode was electrochemically polarized.

The electrode consists of a polycrystalline, 4-6 micron thin film of diamond deposited on a silicon wafer (~ 50 micron); the diamond is heavily doped with boron (~ 6000 ppm). The electrode is pressed onto a ZnSe ATR crystal with the silicon side in contact with the crystal; electrolyte (0.5 M H_2SO_4) is in contact with the diamond film (Figure 1). Infrared enters through the ZnSe crystal and passes through the transparent silicon and diamond layers where it internally reflects at the diamond-electrolyte interface. We then electrochemically polarize the electrode and observe IR changes in the double layer region as well as the termination of the diamond surface as a function of polarization voltage.

Before polarization, the IR spectra clearly show the presence of water and H_2SO_4 bands of the electrolyte. During voltammetry, as the electrochemical polarization increases from 0.0 V (vs. SHE) to 3.0 V, an OH stretch feature appears in the IR spectrum at 3240 cm^{-1} and increases with voltage. We have assigned it to the formation of -OH groups on the diamond surface. An additional feature appears at 1100 cm^{-1} which is consistent with the CO stretch (Figure 2).

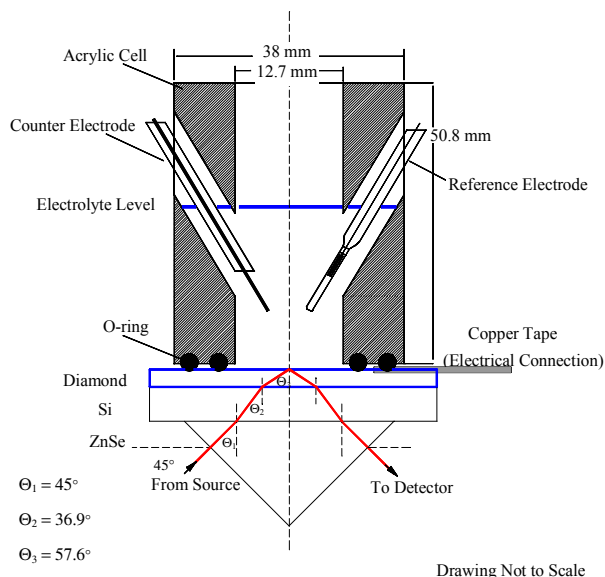


Figure 1 – Schematic diagram of the spectro-electrochemical cell. Note that the diamond thin film is $4\text{--}6\text{ }\mu\text{m}$ thick and the silicon wafer is $\sim 50\text{ }\mu\text{m}$ thick.

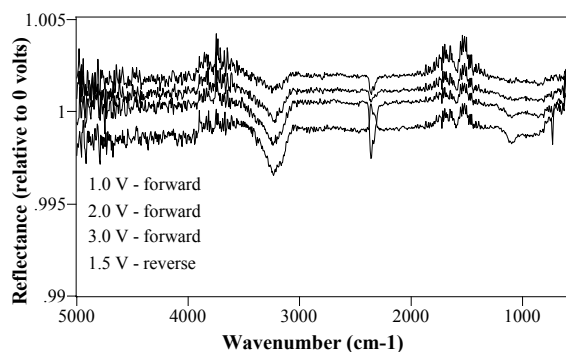


Figure 2 – Infrared spectra taken during step-wise polarization of a conditioned diamond electrode at various potentials. Prior to taking these spectra, the electrode is conditioned with at least 10 minutes of cyclic voltammetry. Note that the spectra are on the same scale, but offset for clarity. The feature at 3240 cm^{-1} is assigned to O-H stretch while the feature at 1100 cm^{-1} is assigned to C-O stretch. The other features are due to atmospheric CO_2 (2350 cm^{-1}) and water vapor (1600 and 3750 cm^{-1}) in the IR beam path. The terms forward and reverse refer to the order in which the potential is swept.